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(54) Title: IMPACT-RESISTANT POLYOLEFIN COMPOSITIONS

(57) Abstract: Polyolefin compositions comprising (percent by weight): 1) 55-90% of a crystalline propylene homopolymer or copolymer containing up to 15% of ethylene and/or C<sub>4</sub>-C<sub>10</sub> α-olefin(s) and having values of MFR equal to or higher than 25 g/10 min; 2) 10-45% of a copolymer of ethylene with one or more C<sub>4</sub>-C<sub>10</sub> α-olefin(s) containing from 10 to 40% of said C<sub>4</sub>-C<sub>10</sub> α-olefin(s); said compositions having values of MFR equal to or higher than 20 g/10 min, a total content of ethylene of 20% or more, a total content of C<sub>4</sub>-C<sub>10</sub> α-olefin(s) of 4.5% or more, a ratio of the total content of ethylene to the total content of C<sub>4</sub>-C<sub>10</sub> α-olefin(s) of 2.3 or more, a total fraction soluble in xylene at room temperature of less than 18 wt% and an intrinsic viscosity value of the fraction soluble in xylene at room temperature of 1.7 dl/g or less.



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## IMPACT-RESISTANT POLYOLEFIN COMPOSITIONS

The present invention concerns polyolefin compositions comprising a crystalline propylene polymer component selected from propylene-ethylene and/or other  $\alpha$ -olefin random copolymers, and a copolymer of ethylene with C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefins.

The compositions of the present invention can be easily converted into various kinds of finished or semi-finished articles, in particular by using injection-moulding techniques, as they exhibit relatively high values of melt flow rate (MFR). In addition, as the said compositions generally show substantially no stress whitening when bending a 1 mm thick plaque, they can be used for several applications, including housewares and toys, and in particular for food-contact applications.

Compositions comprising polypropylene and a rubbery phase formed by an elastomeric copolymer of ethylene with  $\alpha$ -olefins are already known in the art, and described in particular in European patents 170 255 and 373 660, and in WO 01/19915. Said compositions exhibit impact resistance and, in the case of European patent 373 660 and WO 01/19915, transparency values interesting for many applications, however the overall balance of properties is still not totally satisfactory in the whole range of possible applications, in view of the high standards required by the market. Therefore there is a continuous demand for compositions of this kind with improved properties.

A new and valuable balance of properties has now been achieved by the polyolefin compositions of the present invention, comprising (percent by weight):

- 1) 55-90% of a crystalline propylene homopolymer or copolymer containing up to 15% of ethylene and/or C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) and having a value of MFR (230 °C, 2.16 kg) of at least 25 g/10 min; and
- 2) 10-45% of a copolymer of ethylene with one or more C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) containing from 10 to 40% of said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s), preferably from 10 to 35%, of said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s);

said compositions having values of MFR equal to or higher than 20 g/10 min, a total content of ethylene of 20% or more, preferably 22% or more, a total content of C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) of 4.5% or more, a ratio of the total content of ethylene to the total content of C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) of 2.3 or more, preferably of 2.5 or more, a total fraction soluble in xylene at room temperature of less than 17 wt% and an intrinsic viscosity value of the fraction soluble in xylene at room temperature of 1.7 dl/g or less, preferably of 1.5 dl/g or less.

From the above definitions it is evident that the term "copolymer" includes polymers containing more than one kind of comonomers.

As previously said, the compositions of the present invention can be easily converted into various kinds of finished or semi-finished articles, in particular by using injection-molding techniques, as they exhibit relatively high values of MFR, associated with the said high balance of properties (in particular, of flexural modulus, impact resistance, ductile/brittle transition temperature and haze).

In addition they exhibit low or very low blush, reduced blooming and low content of fraction extractable in organic solvents.

Other preferred features for the compositions of the present invention are:

- content of polymer insoluble in xylene at room temperature (23 °C) (substantially equivalent to the Isotacticity Index) for component 1): not less than 90%, in particular not less than 93%, said percentages being by weight and referred to the weight of component 1);
- a total content of ethylene from 20% to 40% by weight;
- a total content of C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) from 5.5% to 15% by weight ;
- a flexural modulus from 770 to 1400 MPa;
- fraction soluble in xylene at room temperature: preferably less than 15% by weight;
- intrinsic viscosity of the fraction soluble in xylene at room temperature in the range from 0.8 to 1.5 dl/g.

The ductile/brittle transition temperature is generally equal to or lower than -25 °C, preferably lower than -30°C; the lowest limit being indicatively of about -60 °C.

The compositions of the present invention have preferably an MFR value of 25 g/10 min or higher, for example in the range from 25 to 60 g/10 min.

The said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefins, which are or may be present as comonomers in the components and fractions of the compositions of the present invention, are represented by the formula CH<sub>2</sub>=CHR, wherein R is an alkyl radical, linear or branched, with 2-8 carbon atoms or an aryl (in particular phenyl) radical.

Examples of said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefins are 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene. Particularly preferred is 1-butene.

The compositions of the present invention can be prepared by a sequential polymerization, comprising at least two sequential steps, wherein components 1) and 2) are

prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step. The catalyst is added only in the first step, however its activity is such that it is still active for all the subsequent steps.

Preferably component 1) is prepared before component 2).

The polymerization, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques. Preferably both components 1) and 2) are prepared in gas phase.

Reaction time, pressure and temperature relative to the two steps are not critical, however it is best if the temperature is from 20 to 100 °C. The pressure can be atmospheric or higher.

The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

Such polymerization is preferably carried out in the presence of stereospecific Ziegler-Natta catalysts. An essential component of said catalysts is a solid catalyst component comprising a titanium compound having at least one titanium-halogen bond, and an electron-donor compound, both supported on a magnesium halide in active form. Another essential component (co-catalyst) is an organoaluminum compound, such as an aluminum alkyl compound.

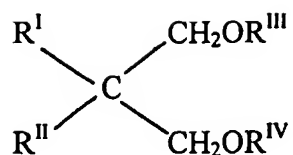
An external donor is optionally added.

The catalysts generally used in the process of the invention are capable of producing polypropylene with an isotactic index greater than 90%, preferably greater than 95%. Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in US patent 4,399,054 and European patent 45977.

The solid catalyst components used in said catalysts comprise, as electron-donors (internal donors), compounds selected from the group consisting of ethers, ketones, lactones, compounds containing N, P and/or S atoms, and esters of mono- and dicarboxylic acids.

Particularly suitable electron-donor compounds are phthalic acid esters, such as diisobutyl, dioctyl, diphenyl and benzylbutyl phthalate.

Other electron-donors particularly suitable are 1,3-diethers of formula:



wherein R<sup>I</sup> and R<sup>II</sup> are the same or different and are C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>18</sub> cycloalkyl or C<sub>7</sub>-C<sub>18</sub> aryl radicals; R<sup>III</sup> and R<sup>IV</sup> are the same or different and are C<sub>1</sub>-C<sub>4</sub> alkyl radicals; or are the 1,3-diethers in which the carbon atom in position 2 belongs to a cyclic or polycyclic structure made up of 5, 6 or 7 carbon atoms and containing two or three unsaturations.

Ethers of said type are described in published European patent applications 361493 and 728769.

Representative examples of said dieters are 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isoamyl-1,3-dimethoxypropane, 9,9-bis (methoxymethyl) fluorene.

The preparation of the above mentioned catalyst components is carried out according to various methods.

For example, a MgCl<sub>2</sub>·nROH adduct (in particular in the form of spheroidal particles) wherein n is generally from 1 to 3 and ROH is ethanol, butanol or isobutanol, is reacted with an excess of TiCl<sub>4</sub> containing the electron-donor compound. The reaction temperature is generally from 80 to 120 °C. The solid is then isolated and reacted once more with TiCl<sub>4</sub>, in the presence or absence of the electron-donor compound, after which it is separated and washed with aliquots of a hydrocarbon until all chlorine ions have disappeared.

In the solid catalyst component the titanium compound, expressed as Ti, is generally present in an amount from 0.5 to 10% by weight. The quantity of electron-donor compound which remains fixed on the solid catalyst component is generally 5 to 20% by moles with respect to the magnesium dihalide.

The titanium compounds which can be used for the preparation of the solid catalyst component are the halides and the halogen alcoholates of titanium. Titanium tetrachloride is the preferred compound.

The reactions described above result in the formation of a magnesium halide in active form. Other reactions are known in the literature, which cause the formation of magnesium halide in active form starting from magnesium compounds other than halides, such as magnesium carboxylates.

The Al-alkyl compounds used as co-catalysts comprise the Al-trialkyls, such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O or N atoms, or SO<sub>4</sub> or SO<sub>3</sub> groups.

The Al-alkyl compound is generally used in such a quantity that the Al/Ti ratio be from 1 to 1000.

The electron-donor compounds that can be used as external donors include aromatic acid esters such as alkyl benzoates, and in particular silicon compounds containing at least one Si-OR bond, where R is a hydrocarbon radical.

Examples of silicon compounds are (tert-butyl)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (cyclohexyl)(methyl)Si(OCH<sub>3</sub>)<sub>2</sub>, (phenyl)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub> and (cyclopentyl)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>. 1,3-diethers having the formulae described above can also be used advantageously. If the internal donor is one of these diethers, the external donors can be omitted.

The catalysts can be pre-contacted with small amounts of olefins (prepolymerization).

Other catalysts that may be used in the process according to the present invention are metallocene-type catalysts, as described in USP 5,324,800 and EP-A-0 129 368; particularly advantageous are bridged bis-indenyl metallocenes, for instance as described in USP 5,145,819 and EP-A-0 485 823. Another class of suitable catalysts are the so-called constrained geometry catalysts, as described in EP-A-0 416 815 (Dow), EP-A-0 420 436 (Exxon), EP-A-0 671 404, EP-A-0 643 066 and WO 91/04257. These metallocene compounds may be used in particular to produce the copolymers (a) and (b).

The compositions of the present invention can also be obtained by preparing separately the said components 1) and 2), by operating with the same catalysts and substantially under the same polymerization conditions as previously explained (except that a wholly sequential polymerization process will not be carried out, but the said components will be prepared in separate polymerization steps) and then mechanically blending said components in the molten or softened state. Conventional mixing apparatuses, like screw extruders, in particular twin screw extruders, can be used.

The compositions of the present invention can also contain additives commonly employed in the art, such as antioxidants, light stabilizers, heat stabilizers, nucleating agents, colorants and fillers.

In particular, the addition of nucleating agents brings about a considerable improvement in important physical-mechanical properties, such as flexural modulus, Heat Distortion

Temperature (HDT), tensile strength at yield and transparency.

Typical examples of nucleating agents are the p-tert.-butyl benzoate and the 1,3- and 2,4-dibenzylidenesorbitols.

The nucleating agents are preferably added to the compositions of the present invention in quantities ranging from 0.05 to 2% by weight, more preferably from 0.1 to 1% by weight with respect to the total weight.

The addition of inorganic fillers, such as talc, calcium carbonate and mineral fibers, also brings about an improvement to some mechanical properties, such as flexural modulus and HDT. Talc can also have a nucleating effect.

The particulars are given in the following examples, which are given to illustrate, without limiting, the present invention.

#### **Examples 1-7**

In the following examples polyolefin compositions according to the present invention are prepared by sequential polymerization.

The solid catalyst component used in polymerization is a highly stereospecific Ziegler-Natta catalyst component supported on magnesium chloride, containing about 2.5% by weight of titanium and diisobutylphthalate as internal donor, prepared by analogy with the method described in Example 1 of European published patent application 674991.

#### **CATALYST SYSTEM AND PREPOLYMERIZATION TREATMENT**

Before introducing it into the polymerization reactors, the solid catalyst component described above is contacted at -5 °C for 5 minutes with aluminum triethyl (TEAL) and dicyclopentyldimethoxysilane (DCPMS), in a TEAL/DCPMS weight ratio equal to about 4 and in such quantity that the TEAL/Ti molar ratio be equal to 65.

The catalyst system is then subjected to prepolymerization by maintaining it in suspension in liquid propylene at 20 °C for about 20 minutes before introducing it into the first polymerization reactor.

#### **POLYMERIZATION**

The polymerization is carried out in continuous in a series of two gas phase reactors equipped with devices for the transfer of the product coming from the reactor immediately preceding to the one immediately following.

In gas phase the hydrogen and the monomer(s) are analyzed in continuous and fed in such a manner that the desired concentration be maintained constant.

Into a first gas phase polymerization reactor a propylene/ethylene copolymer is produced by feeding in a continuous and constant flow the prepolymerized catalyst system, hydrogen (used as molecular weight regulator) and propylene and ethylene monomers in the gas state, thus obtaining component 1). The polymerization temperature is 80° C.

The polymer produced in the first reactor is discharged in the second reactor where an ethylene/butene copolymer is produced by feeding the monomer(s) and hydrogen in proper molar ratios, thus obtaining component 2).

Then the polymer particles are introduced in a rotating drum, where they are mixed with 0.05% by weight of paraffinic oil, 0.05% by weight of sodium stearate, 0.15% by weight of Irganox® B215 (1 weight part of pentaerithryl-tetrakis[3(3,5-di-tert-butyl-4-hydroxyphenyl)] mixed with 1 weight part of tris(2,4-ditert-butylphenyl) phosphite) and 0.18% by weight of Millad® 3988 3,4-dimethylbenzylidene sorbitol.

Then the polymer particles are introduced in a twin screw extruder Berstorff™ ZE 25 (length/diameter ratio of screws: 33) and extruded under nitrogen atmosphere in the following conditions:

Rotation speed: 250 rpm;  
Extruder output: 6-20 kg/hour;  
Melt temperature: 200-250 °C.

The data relating to the final polymer compositions reported in tables 1 and 2 are obtained from measurements carried out on the so extruded polymers.

The data shown in the tables are obtained by using the following test methods.

- **Molar ratios of the feed gases**

Determined by gas-chromatography.

- **Ethylene and 1-butene content of the polymers**

Determined by I.R. spectroscopy.

- **Melt Flow Rate (MFR)**

Determined according to ASTM D 1238, condition L (MFR“L”).

- **Xylene soluble and insoluble fractions**

Determined as follows.

2.5 g of polymer and 250 ml of xylene are introduced in a glass flask equipped with a refrigerator and a magnetical stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The so obtained clear solution is then kept under reflux and



stirring for further 30 minutes. The closed flask is then kept for 30 minutes in a bath of ice and water and in thermostatic water bath at 25 °C for 30 minutes as well. The so formed solid is filtered on quick filtering paper. 100 ml of the filtered liquid is poured in a previously weighed aluminum container which is heated on a heating plate under nitrogen flow, to remove the solvent by evaporation. The container is then kept in an oven at 80 °C under vacuum until constant weight is obtained. The weight percentage of polymer soluble in xylene at room temperature is then calculated. The percent by weight of polymer insoluble in xylene at room temperature is considered the Isotacticity Index of the polymer. This value corresponds substantially to the Isotacticity Index determined by extraction with boiling n-heptane, which by definition constitutes the Isotacticity Index of polypropylene.

- **Intrinsic Viscosity (I.V.)**

Determined in tetrahydronaphthalene at 135 °C.

- **Flexural Modulus**

Determined according to ISO 178.

- **Ductile/Brittle transition temperature (D/B)**

Determined according to internal method MA 17324, available upon request.

According to this method, the bi-axial impact resistance is determined through impact with an automatic, computerised striking hammer.

The circular test specimens are obtained by cutting with circular hand punch (38 mm diameter). They are conditioned for at least 12 hours at 23°C and 50 RH and then placed in a thermostatic bath at testing temperature for 1 hour.

The force-time curve is detected during impact of a striking hammer (5.3 kg, hemispheric punch with a 1.27 cm diameter) on a circular specimen resting on a ring support. The machine used is a CEAST 6758/000 type model No. 2.

D/B transition temperature means the temperature at which 50% of the samples undergoes fragile break when submitted to the said impact test.

- **Preparation of the plaque specimens**

Plaques for D/B measurement, having dimensions of 127×127×1.5 mm are prepared according to internal method MA 17283; plaques for haze measurement, 1 mm thick, are prepared by injection moulding according to internal method MA 17335 with injection time of 1 second, temperature of 230 °C, mould temperature of 40 °C, description of all

the said methods being available upon request.

**Method MA 17283**

The injection press is a Negri Bossi™ type (NB 90) with a clamping force of 90 tons. The mould is a rectangular plaque (127×127×1.5 mm).

The main process parameters are reported below:

Back pressure (bar):	20
Injection time (s):	3
Maximum Injection pressure (MPa):	14
Hydraulic injection pressure (MPa):	6-3
First holding hydraulic pressure (MPa):	4±2
First holding time (s):	3
Second holding hydraulic pressure (MPa):	3±2
Second holding time (s):	7
Cooling time (s):	20
Mould temperature (°C):	60

The melt temperature is between 220 and 280 °C.

**Method MA 17335**

The injection press is a Battenfeld™ type BA 500CD with a clamping force of 50 tons.

The insert mould leads to the moulding of two plaques (55×60×1 or 1.5 mm each).

- **Haze on plaque**

Determined according to internal method MA 17270, available upon request.

The plaques are conditioned for 12 to 48 hours at relative humidity of 50±5% and temperature of 23±1° C.

The apparatus used is a Hunter™ D25P-9 colorimeter. The measurement and computation principle are given in the norm ASTM-D1003.

The apparatus is calibrated without specimen, the calibration is checked with a haze standard. The haze measurement is carried out on five plaques.

- **Izod impact strength (notched)**

Determined according to ISO180/1A.

**Comparative example 1c**

Example 1 is repeated except that the polymerisation is carried out in a series of three reactors. Into the first reactor a crystalline propylene-ethylene copolymer is produced

feeding the monomers and hydrogen in proper molar ratios (component (A')). The copolymer thus produced is discharged into the second reactor where a propylene-ethylene copolymer is produced by feeding the monomers and hydrogen in proper molar ratios (component (A'')).

The copolymer produced in the second reactor is discharged in a continuous flow and, after having being purged of unreacted monomers, is introduced in a continuous flow into the third gas phase reactor, together with quantitatively constant flows of hydrogen and ethylene and 1-butene monomers in the gas state. Component (B) is thus obtained.

Polymerisation conditions, molar ratios, composition and properties of the copolymers obtained are shown in table 2. The comparative composition shows a value of flexural modulus in the same range as the one of the compositions of the present invention, value which is obtained only thanks to a crystalline polymer moiety of the matrix having a low flowability.

In comparison with the comparative composition, the compositions according to the present invention have a comparable or even better stiffness and better impact resistance in terms of ductile/brittle transition temperature in spite of remarkably higher MFR values that improve workability as it generally affects stiffness and impact resistance.

TABLE 1

Example		1	2	3
<b>1<sup>st</sup> Gas Phase Reactor - crystalline propylene-ethylene copolymer</b>				
Split	wt%	67	65	65
MFR "L"	g/10'	70.5	97	49.9
Ethylene content in the copolymer	wt%	3.0	2.8	2.8
Xylene soluble fraction	wt%	4.2	4.3	4.2
<b>2<sup>nd</sup> Gas Phase Reactor - ethylene-butene-1 copolymer rubber</b>				
Temperature	°C	75	75	75
Split	wt%	33	35	35
Butene-1 in the rubber	wt%	14	16	15
Xylene-soluble fraction	wt%	34	39	38
<b>Final Product</b>				
MFR "L"	g/10'	28.7	48.4	27.5
Xylene-soluble fraction	wt%	13.9	16.5	16.1
I.V. of the xylene-soluble fraction	dl/g	1.25	1.1	1.11
Ethylene content	wt%	30.6	31.1	31.6
Butene-1 content	wt%	4.7	5.9	5.4
Flexural modulus	MPa	775	800	805
D/B transition temperature	°C	-50	-54	-50
Izod impact resistance at 23° C	kJ/m <sup>2</sup>	7.2	5.7	7.2
Haze, 1 mm plaque	%	27	27.8	25.7

TABLE 2

Example and comparative example		4	5	6	7	1c
<b>1<sup>st</sup> Gas Phase Reactor - crystalline propylene-ethylene copolymer</b>						
Split	wt%	72	75	72	72	39
MFR "L"	g/10'	38.3	41.5	83	42.4	1.2
H <sub>2</sub> /C <sub>3</sub>	mol					0.002
Ethylene content in the copolymer	wt%	1.7	1.4	0	0	2.6
Xylene-soluble fraction	wt%	1.9	1.7	1.4	1.4	-
<b>2<sup>nd</sup> Gas Phase Reactor - crystalline propylene-ethylene copolymer</b>						
Split	wt%	0	0	0	0	39
MFR "L" (total)	g/10'	-	-	-	-	11.7
Ethylene content in the copolymer	wt%	-	-	-	-	2.6
H <sub>2</sub> /C <sub>3</sub>	mol	-	-	-	-	0.419
Xylene-soluble fraction (total)	wt%	-	-	-	-	96.5
<b>2<sup>nd</sup>/3<sup>rd</sup> Gas Phase Reactor - ethylene-butene-1 copolymer rubber</b>						
Temperature	°C	75	65	65	65	70
Split	wt%	28	25	28	28	22
Butene-1 in the rubber	wt%	24	21	21	21	23.6
Xylene-soluble fraction	wt%	58	52	51	51	-
<b>Final Product</b>						
MFR "L"	g/10'	25.1	29.1	47.3	32.2	9.4
Xylene-soluble fraction	wt%	17.6	14.2	14.7	15.2	13.6
I.V. of the xylene-soluble fraction	dl/g	1.37	1.1	1.12	1.08	1.29
Ethylene content	wt%	22	21.2	22.1	21.9	18.4
Butene-1 content	wt%	6.4	5.3	5.5	5.8	5.2
Flexural modulus	MPa	960	1190	1430	1340	1015
D/B transition temperature	°C	-43	-27	-39	-36	-22
Izod impact strength at 23°C	kJ/m <sup>2</sup>	7.2	4.4	3.9	4.1	-
Haze, 1 mm plaque	%	23.4	18.8	28.8	27	13.3

Notes to the tables. Split: weight fraction of polymer produced in the specified reactor; C<sub>3</sub>: propylene

## CLAIMS

1. Polyolefin compositions comprising (percent by weight):
  - 1) 55-90% of a crystalline propylene homopolymer or copolymer containing up to 15% of ethylene and/or C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) and having a value of MFR (230 °C, 2.16 kg) of at least 25 g/10 min; and
  - 2) 10-45% of a copolymer of ethylene with one or more C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) containing from 10 to 40% of said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s);said compositions having values of MFR equal to or higher than 20 g/10 min, a total content of ethylene of 20% or more, a total content of C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) of 4.5% or more, a ratio of the total content of ethylene to the total content of C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) of 2.3 or more, a total fraction soluble in xylene at room temperature of less than 18 wt% and an intrinsic viscosity value of the fraction soluble in xylene at room temperature of 1.7 dl/g or less.
2. The polyolefin compositions of claim 1, having MFR values equal to or higher than 25 g/10 min.
3. The polyolefin compositions of claim 1, wherein the intrinsic viscosity of the fraction soluble in xylene at room temperature is in the range from 0.8 to 1.5 dl/g.
4. The polyolefin compositions of claim 1, wherein the content of polymer soluble in xylene at room temperature is less than 25%.
5. The polyolefin compositions of claim 1, having a Ductile/Brittle transition temperature equal to or lower than -35 °C.
6. A process for producing the polyolefin compositions of claim 1, carried out in at least two sequential steps, wherein in at least one polymerization step the relevant monomer(s) are polymerized to form component 1) and in the other step the relevant monomers are polymerized to form component 2), operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step.
7. The process of claim 6, wherein the polymerization catalyst is a stereospecific Ziegler-Natta catalyst comprising, as catalyst-forming components, a solid component comprising a titanium compound having at least one titanium-halogen bond and an electron-donor compound, both supported on a magnesium halide in active form, and an organoaluminum compound.

8. The process of claim 6, wherein both components 1) and 2) are prepared in gas phase.
9. Injection moulded articles comprising the polyolefin compositions of claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP 03/06093

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/10 B29C45/00 //(C08L23/10,23:08)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 541 260 A (PELLICONI ANTEO ET AL) 30 July 1996 (1996-07-30)	1,3-9
Y	abstract column 1, line 5 -column 3, line 40; examples; tables 2-4	1-9
Y	US 4 734 459 A (CECCHIN GIULIANO ET AL) 29 March 1988 (1988-03-29) cited in the application abstract column 1, line 6 -column 2, line 46; tables I-II --- -/--	1-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 September 2003

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## INTERNATIONAL SEARCH REPORT

PCT/EP 03/06093

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 936 248 A (TOYOTA MOTOR CO LTD ; GRAND POLYMER CO LTD (JP)) 18 August 1999 (1999-08-18) abstract page 1, line 5 -page 2, line 19 page 2, line 50 - line 55 examples; tables 1-8 page 8, line 24 - line 41 ----	1-9
A	WO 01 19915 A (FERRARI PAOLO ; PELLICONI ANTEO (IT); SGARZI PAOLA (IT); CECCHIN GI) 22 March 2001 (2001-03-22) cited in the application abstract column 1, line 9 -column 3, line 52; examples; tables 1,2 -----	1-9

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5541260	A	30-07-1996	IT 1256663 B 12-12-1995
			AT 140947 T 15-08-1996
			AU 667410 B2 21-03-1996
			AU 5236493 A 30-06-1994
			DE 69303881 D1 05-09-1996
			DE 69303881 T2 16-01-1997
			EP 0603723 A1 29-06-1994
			ES 2090829 T3 16-10-1996
			JP 7003087 A 06-01-1995
			MX 9307889 A1 29-07-1994
US 4734459	A	29-03-1988	IT 1206128 B 14-04-1989
			AT 46353 T 15-09-1989
			AU 582175 B2 16-03-1989
			AU 4555885 A 06-02-1986
			CA 1276350 C 13-11-1990
			DE 3572989 D1 19-10-1989
			EP 0170255 A1 05-02-1986
			ES 8700294 A1 01-01-1987
			JP 7042366 B 10-05-1995
			JP 61042553 A 01-03-1986
			NO 852996 A , B, 31-01-1986
EP 0936248	A	18-08-1999	JP 11228782 A 24-08-1999
			AU 745801 B2 11-04-2002
			AU 1643799 A 02-09-1999
			DE 69906845 D1 22-05-2003
			EP 0936248 A1 18-08-1999
			US 6121363 A 19-09-2000
WO 0119915	A	22-03-2001	AU 7517000 A 17-04-2001
			BR 0007075 A 10-07-2001
			CA 2349297 A1 22-03-2001
			CN 1321178 T 07-11-2001
			CZ 20012131 A3 13-03-2002
			WO 0119915 A1 22-03-2001
			EP 1135440 A1 26-09-2001
			HU 0104592 A2 28-03-2002
			JP 2003509562 T 11-03-2003
			NO 20012326 A 11-05-2001
			PL 347656 A1 22-04-2002
			TR 200101320 T1 21-12-2001
			US 6441094 B1 27-08-2002